

Thermodynamic and Experimental Study on Alcohol Made by Synthesis Gas

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Abstract: First C₁-C₅ alcohols which were very important in practical application were analyzed, and the thermodynamic analysis for the synthesis of C₁-C₅ alcohols can guide the experiment in praxis. In the article the equilibrium constants were used to analyze the thermodynamic of the synthesis of C₁-C₅ alcohols and verified the calculation results in line with the trends of theoretical analysis. Reducing temperature and raising the pressure is useful for CO conversion rate and the generation of C₁-C₅ alcohols, as well as different molar ratio of H₂/CO influence CO conversion rate. Eventually the optimum condition was confirmed. A new type of catalyst was developed, which can increase the yield of alcohols, then the theoretical analysis's correctness are verified by the experimental data.

Key words: Syngas, C₁-C₅ Alcohols, Thermodynamic, catalyst

I. INTRODUCTION

With the decrease of oil resource and enhancement of environmental consciousness, the synthesis of C₁-C₅ alcohols from coal, natural gas and organic waste has become one of the important research contents of C₁ chemical. The main application of liquid fuel represented by C₁-C₅ alcohols is used as pure gasoline additives C₁-C₅ alcohols, as we define it here, is mainly based on ethanol and partly based on C₂⁺ alcohol) and a kind of clean fuel alone[1].

The thermodynamic analysis of chemical reaction system is mainly consisted of two contents: one is energy exchange in the process of chemical reaction; the other is chemical equilibrium analysis. However, chemical equilibrium is an ideal state of the reaction that any actual system can't achieve but closer and closer. The equilibrium conversion is a target

actually used to measure the process of chemical reaction. Chemical equilibrium analysis is still very important for understanding characteristics of the reaction during development [2]: Test parameters can be determined by the equilibrium conversion of research system and relationship between product distributions and reaction condition (temperature, pressure, raw material proportion) in state of chemical equilibrium.

Although there are a lot of thermodynamics researches in C₁-C₅ alcohols from synthesis gas [3-6], it still lacks of systematization under the current reaction conditions. This article analyses and calculate thermodynamics trend under different parameters in the synthesis of alcohol and validate it by test.

II. MECHANISM ANALYSIS OF C₁-C₅ ALCOHOLS FROM SYNGAS

According to literature [6], thermodynamics data of C₁-C₅ alcohols from CO and H₂ is given in Table 1.

Figure 1. TAB 1 THERMODYNAMIC DATA

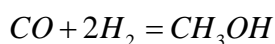
Reaction formula	$\Delta G_{298/K}$ J • mol ⁻¹	K _p
CO+2H ₂ →CH ₃ OH(g)	-41.22	1.67×10 ⁶
2CO+4H ₂ →CH ₃ CH ₂ OH(g)+H ₂ O(g)	-126.90	1.71×10 ²²
3CO+6H ₂ →CH ₃ CH ₂ CH ₂ OH(g)+2H ₂ O(g)	-212.60	1.76×10 ³⁷

Whether the reaction under certain condition can carry on mainly distinguish by free energy ΔG_0 of that reaction. All in all, higher ΔG_0 is going against the reaction under given conditions. According to Table 1, the synthesis of low carbon

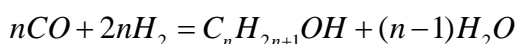
number alcohol is easier to carry on than the high one. That is to say, the alcohol content of high carbon number is lower than the low one in equilibrium. Analyzed from the thermodynamics, the ethanol synthesis from CO Hydrogenation can be carried out. It is a chemical reaction accompanied by the evolution of heat and decrease of mole number. Too high temperature is disadvantageous to it and pressure processes can effectively accelerates the reaction. Therefore the ethanol synthesis from CO Hydrogenation is carry on under relative low temperature and high pressure.

A. Reaction Principle

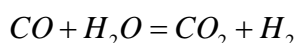
It is quite complicated reaction that mixed alcohols of low carbon form syngas of H_2 and CO mainly consist of synthesis, synthesis of C_1 - C_5 alcohols, water-gas shift reaction and so on [7].



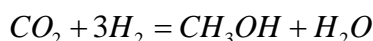
$$\Delta G^0 = -27.288 + 0.05838T$$



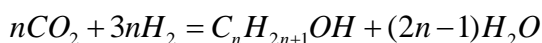
$$\Delta G^0 = -38.386n + 38.158 + (5.982n - 0.114) \times 10^{-2}T$$



$$\Delta G^0 = -8.154 + 0.771 \times 10^{-2}T$$



$$\Delta G^0 = -18.774 + 5.067 \times 10^{-2}T$$



$$\Delta G^0 = -29.872n + 35.158 + (5.211n - 0.114) \times 10^{-2}T$$

B. Algorithm

The algorithms of chemical equilibrium have two classes, solving the composition when system free energy reach minimum by optimization on the premise of atom balance called minimum free energy algorithm [8] and solving the chemical equilibrium equation called equilibrium constant algorithm [9]. Some pundit [6] has made thermodynamic analysis of the alcohol synthesis under different conditions by minimum free energy algorithm. Nevertheless, present conditions of the synthesis have great differences. The most difference is temperature, the initial temperature was then 613K, but now it is not usually exceed 573K. This paper

calculate K_p at different pressure (1Mpa~8Mpa) and temperature (500K~650K) by equilibrium constant algorithm. And then, solving each substance constituents by K_p when it achieve chemical equilibrium at corresponding conditions. Furthermore, investigate the conversion of CO at different mole ratio m ($m=1.5, 2.0, 2.5$) between CO and H_2 and the selectivity of alcohols at equilibrium state.

The main factors influencing thermodynamic equilibrium include temperature, pressure and inert gases. We are going to analyze each factor and the gas is considered as ideal in standard state. The basic thermodynamic data of each constituent and formulas are found [10, 11].

The system will be equilibrium when amount of each substance remained unchanged. For ideal gas,

$$K_p^\theta = K_f^\theta,$$

$$K_f^\theta = K_p^\theta = \frac{\left(\frac{p_G}{p^\theta}\right)^g \left(\frac{p_H}{p^\theta}\right)^h}{\left(\frac{p_D}{p^\theta}\right)^d \left(\frac{p_E}{p^\theta}\right)^e} = \frac{p_G^g p_H^h}{p_D^d p_E^e} (p^\theta)^{-\sum_B \nu_B} \quad (1)$$

Pressure equilibrium constant K_p :

$$K_f^\theta = K_p K_\gamma (p^\theta)^{-\sum_B \nu_B}, \quad K_p = \prod_B p^{\nu_B}, \quad K_\gamma = \prod_B \gamma^{\nu_B} \quad (2)$$

According to equation $\sum_B \nu_B \mu_B^\theta(T) = \Delta_r G_m^\theta(T) = -RT \ln K_f^\theta$, K_p is relevant to temperature and pressure.

Molar equilibrium constant K_x :

For ideal gas $p_B = p x_B$:

$$K_x = \frac{x_G^g x_H^h \dots}{x_D^d x_E^e \dots} = K_p p^{\sum \nu_B}$$

(3)

It shows that K_x is relevant to temperature and pressure.

Concentration equilibrium constant K_c :

For ideal gas, $p = cRT$,

get

$$K_c(RT)^{\sum \nu_B} = \frac{(c_G RT)^g (c_H RT)^h \dots}{(c_D RT)^d (c_E RT)^e \dots} = \frac{p_G^g p_H^h \dots}{p_D^d p_E^e \dots} = K_p$$

(4)

It is know that, for ideal gas, K_c is the function of temperature.

The solution of K_p :

Setting gas phase equilibrium under condition of constant temperature and volume as follows

$$\phi_1 = N_d + N_G - N_D^0 = 0$$

$$\phi_2 = N_E + N_G - N_E^0 = 0$$

(5)

Solve by lagrange multiplier

$$\frac{N_G^*}{N_D^* N_E^*} = \frac{q'_G}{q'_D q'_E} = K_N$$

(6)

$$\text{substitute } q' = q \cdot \exp\left(-\frac{\varepsilon_0}{kT}\right) \text{ in (6)}$$

$$\Delta_r H_m^\theta(T) = \Delta H_0 + \int \Delta C_p dT = \Delta H_0 + \Delta aT + \frac{1}{2} \Delta bT^2 + \frac{1}{3} \Delta cT^3 + \dots \quad (11)$$

$$K_c = \frac{C_G^*}{C_D^* C_E^*} = \frac{f_G}{f_D f_E} \exp\left(-\frac{\Delta \varepsilon_0}{kT}\right) \quad (7)$$

For ideal gas

$$K_p = K_c (kT)^{\sum \nu_B} = \frac{f_G}{f_D f_E} \exp\left(-\frac{\Delta \varepsilon_0}{kT}\right) \cdot (kT)^{\sum \nu_B} \quad (8)$$

C. Influence of Temperature, pressure and inert gas on synthesis

1) Influence of Temperature on Equilibrium

According to Gibbs-Helmholtz equation:

$$d \left(\frac{\Delta_r G_m^\theta}{T} \right) = - \frac{\Delta_r H_m^\theta}{T^2} \quad (9)$$

substitute $\Delta_r G_m^\theta = -RT \ln K^\theta$ in above equation, get

$$\frac{d \ln K^\theta}{dT} = \frac{\Delta_r H_m^\theta}{RT^2} \quad (10)$$

where $\Delta_r H_m^\theta$ is isobaric reaction heat when all substances are in the standard state.

Synthesis of C1-C5 alcohols is an exothermic reaction.

$\Delta_r H_m^\theta < 0$, $\frac{d \ln K^\theta}{dT} < 0$, namely, K^θ decreases with increasing temperature, too high temperature is disadvantageous to the reaction. Integrating (10), here must consider the relationship between $\Delta_r H_m^\theta$ and T.

where ΔH_0 is integral constant, substitute (10) as follows:

$$\frac{d \ln K^\theta}{dT} = \frac{\Delta H_0}{RT^2} + \frac{\Delta a}{RT} + \frac{\Delta b}{2R} + \frac{\Delta c}{3R} T + \dots$$

Move and integrate, get

$$\ln K^\theta = \left(\frac{\Delta H_0}{R} \right) \frac{1}{T} + \frac{\Delta a}{R} \ln T + \frac{\Delta b}{2R} T + \frac{\Delta c}{6R} T^2 + \dots + I \quad (12)$$

where I is integral constant, substitute $\Delta_r G_m^\theta = -RT \ln K^\theta$ in above equation, get

$$\Delta_r G_m^\theta = \Delta H_0 - \Delta a T \ln T - \frac{\Delta b}{2} T^2 - \frac{\Delta c}{6} T^3 - \dots - IRT \quad (13)$$

Figure 1 is the influence of temperature on CO conversion:

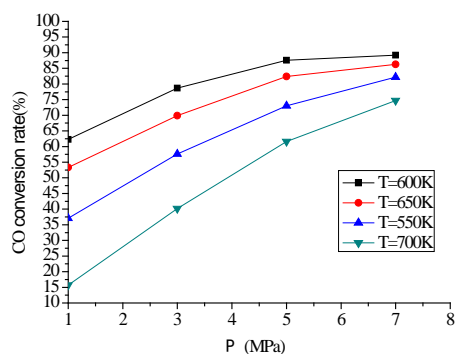


Fig 1 Influence of temperature and pressure on CO conversion rate (m=2.0)

According to figure 1, conversion of CO reduces in a period with the rise of temperature. Fully shows K^θ of alcohols synthesis decreases with increasing temperature and it is an exothermic reaction. Decreasing temperature is advantageous to the yield of alcohols, but it should not be too low, low temperature will cause stopping of reaction. According to free energy ΔG_0 , lower temperature is advantageous to synthesis of high carbon number alcohol and raising temperature is good for generation of low carbon

number alcohol. But higher temperature will accelerate the reaction rate, so reaction temperature selection should consider of all factors comprehensively.

2) Influence of Pressure on Equilibrium

For ideal gas, $K_f^\theta = K_p^\theta$

$$\ln K_p^\theta = - \frac{\sum_B \nu_B \mu_B^\theta(T)}{RT}$$

$$K_p^\theta = K_c^\theta \left(\frac{c^\theta RT}{p^\theta} \right)^{\sum_B \nu_B} = K_x \left(\frac{p}{p^\theta} \right)^{\sum_B \nu_B}$$

$$\text{get } \left(\frac{\partial \ln K_x}{\partial p} \right)_T = 0, \quad \left(\frac{\partial \ln K_c^\theta}{\partial p} \right)_T = 0$$

$$\left(\frac{\partial \ln K_x}{\partial p} \right)_T = - \frac{\sum_B \nu_B}{p} = - \frac{\Delta V_m}{RT} \quad (14)$$

Thus K_x changes with pressure. For synthesis of C1-C5

alcohol, namely $\sum_B \nu_B < 0$, K_x increase with p increasing. It is beneficial for the reaction. Thus pressure process can stimulate the synthesis of C1-C5 alcohol.

In figure 1 we can see the influence of pressure on CO conversion. With pressure increasing, the original higher temperature curve rises faster and low temperature curve rises relatively slowly. It shows that in certain range influence of pressure more than temperature on the reaction. But it is too harsh for mechanical equipment with high pressure, so selecting an appropriate pressure is very important for reaction.

3) Influence of H2/CO Mole Ratio on Equilibrium

Different original gas has great influence on CO conversion. See figure 2 and 3.

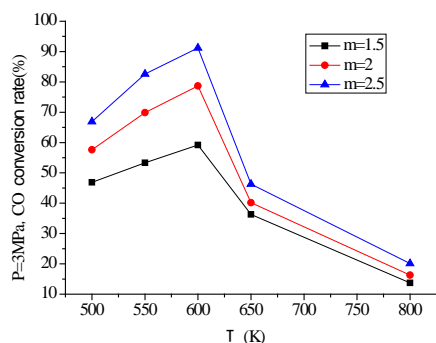


Fig 2. Influence of m on the conversion rate of CO under the pressure of 3MPa

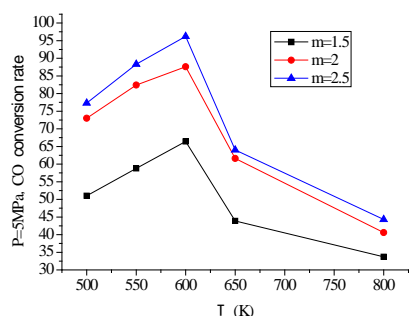


Fig 3 Influence of m on the conversion rate of CO under the pressure of 5MPa

Hydrogen-carbon ratio m is the mole ratio of reaction entrance gas H_2 and CO. According to figure 2 and 3, increase H_2 content of input gas can improve CO conversion. But high content of H_2 will lead to CO too little, thus the content of alcohol too low. Although different m cannot affect the reaction, it will affect equilibrium components in the process of calculation.

III. EXPERIMENT

A. Catalyst Preparation

Making this catalyst aims to overcome the insufficient of existing catalytic systems and provide catalytic for syntheses of C_1 - C_5 alcohols from syngas and its preparation method. This catalyst has higher selectivity of C_2^+ alcohol.

The catalyst expression of syntheses of C_1 - C_5 alcohol from syngas provided by this project is $CuFeCoMAMB/SiO_2$. MA is one or more combination of transition metal elements such as Zn, Cr, Zr, Mn, Mo, Ni, V, Al. MB is one or more

combination of alkaline metal, alkali metal or rare earth elements including Li, Na, K, Ca, Mg, Ba, Ce, etc.

Preparation method of catalyst is impregnating and roasting step by step. Prepare catalyst according to the expression of active components load (wt%) Cu(25) Fe(15) Co(20) MA(15) MB(5). MA is Zn, MB is K_2CO_3 . Confecting nitrate solution of Cu, Fe, Co, Zn according to the proportion of above expression. Take 10.0g 80 mesh microspheres silica gel, impregnating it by two hours at room temperature and drying it at $100^\circ C$. Then, rise temperature to $400^\circ C$ by speed of $1.0^\circ C/min$ and cooling to room temperature naturally after roasting eight hours. Confecting K_2CO_3 solution according to the expression to macerate the samples obtained on first step by 0.5 hours, and then drying it at $100^\circ C$ to obtain the required catalyst.

B. Experimental Process

Drying the catalyst first, grinding it to 80 to 100 meshes and fill into the reactor, and then reducing in hydrogen. Reduction temperature is 400 degrees, reduction time is eight hours and cooling slowly. Put syngas into reaction system through pressure reducing valve, control the pressure between 4 to 6MPa. Control the flow with flowmeter to make molar ratio of H_2/CO reach 2:1. Meanwhile, control airspeed between 3000 and 8000. To make the syngas preheat adequately, fill with quartz sand. The temperature of catalytic reaction of syngas through the last stage can control at 250 to 400 degrees. In order to have enough residence time in catalytic section for syngas, fill the reactor with catalyst which mixed into quartz sand to improve the filling height of catalyst to make the reaction sufficient.

IV. EXPERIMENTAL RESULTS AND ANALYSES

A. Influence of Pressure on Results

Move the catalysts into reactor and reduce it for eight hours with H_2 in $400^\circ C$, then lower the temperature slowly without air. Switch into syngas, pressure is 4.0~6.0MPa, temperature is $350^\circ C$, airspeed is $6000h^{-1}$, $H_2/CO=2$, reaction time is 16h. Collect the liquid product by ice water bath and analyze the composition by gas chromatographic. The results are as follows:

pressure MPa	Space-time yield g/(ml·h)	selectivity of C ₂ ⁺ alcohol %	Alcohol distribution wt%				
			carbinol	ethanol	propanol	butanol	Total
4.0	0.1	5.85	7.84	29.87	21.84	6.78	66.53
4.5	0.22	15.26	8.01	40.32	22.12	6.93	77.38
5.0	0.28	20.82	8.32	46.02	21.34	7.01	82.69
5.5	0.53	40.51	10.56	47.32	21.85	8.27	87
6.0	0.55	43.37	14.83	48.4	22.12	8.33	93.68

As shown in above figures, productivity of C₂⁺ alcohol in low pressure area increase rapidly with pressure increasing, but the tendency slow down beyond certain pressure (5.5Mpa). It is coincide with the trend of theoretical calculation in this chapter that the contents of ethanol, propanol and butanol are increase with pressure increasing. Ethanol increased obviously, the change of propanol and butanol is unconspectuous. When pressure beyond 5.5Mpa, increasing trend of ethanol slow down. It shows that although high pressure is conducive to synthesize and excess pressure can hints synthesis of alcohols compounds, the effect is not obvious. Due to higher requirements for equipment under excess pressure, it is more appropriate for synthesis of alcohol that pressure P=5.5Mpa. It is also coincide with the theoretical calculation.

According to above experimental results, we can obtain trend chart of parameters in the above-said conditions such as CO conversion, C₂⁺ alcohol selectivity, proportion of all kinds C₂⁺ alcohol in the products and so on.

B. Influence of Temperature on Results

Pressure is 5.5MPa, temperature is 280°C~380°C, airspeed is 6000h⁻¹, H₂/CO=2, reaction time is 16h, other parameters are the same. The results are as follows:

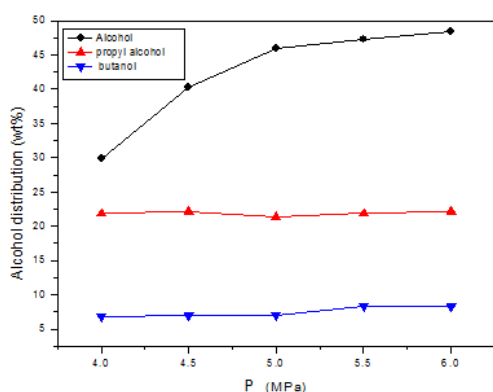


Fig 4 influence of pressure distribution on C₂⁺ alcohols product

tempera ture °C	Space-t ime yield g/(ml·h)	selecti vity of C ₂ ⁺ alcohol %	Alcohol distribution wt%				
			carbi nol	etha nol	propa nol	buta nol	Total alco hol cont ent
280	0.05	2.9	17.75	33.47	17.56	6.93	75.71
300	0.19	13.86	14.37	45.78	19.21	7.96	87.32
350	0.53	40.51	10.56	47.32	20.85	8.27	87
380	0.44	28.46	11.6	37.54	18.59	8.56	76.29

According to above experimental results, we can obtain trend chart of parameters in the above-said conditions such as CO conversion, C₂⁺ alcohol selectivity, proportion of all kinds C₂⁺ alcohol in the products and so on.

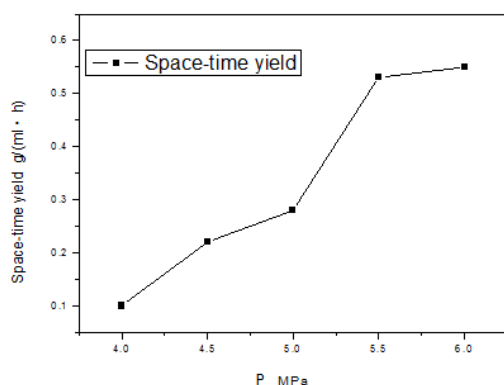
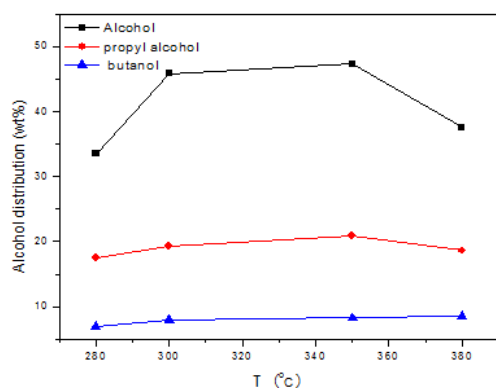
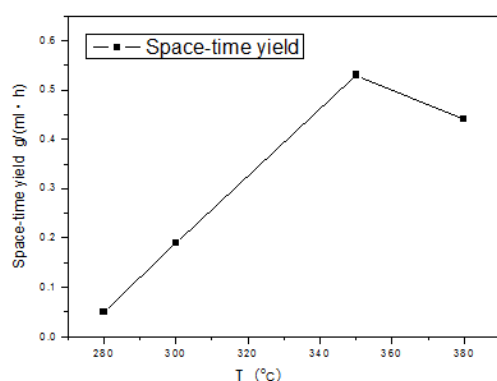


Fig 5 influence of pressure distribution on C₂⁺ alcohols yield

Fig 6 influence of temperature distribution on C_2^+ alcohols productFig 7 influence of pressure distribution on C_2^+ alcohols yield

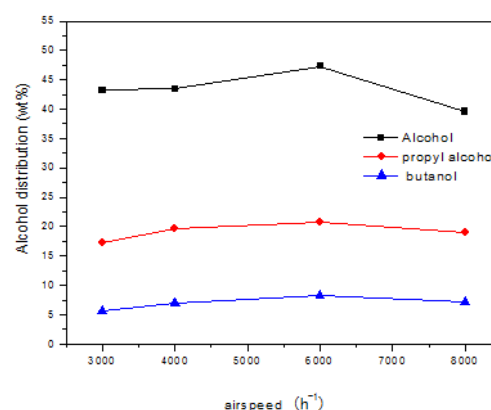
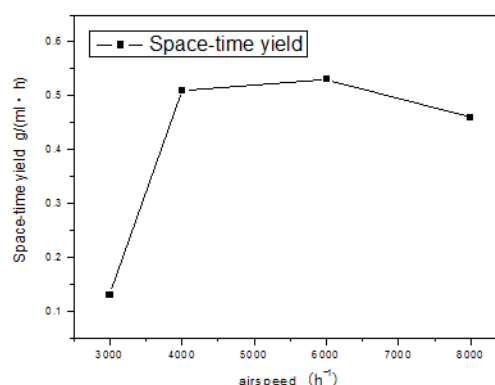
As shown in above figures, ethanol increasing is relatively obvious in early temperatures rising stage. This is due to increasing reaction temperature make the activity of molecule and catalysts strengthened, so alcohol conversion also increase with temperature increasing. Although propanol and butanol increase a little in the process of temperature variation, it is unobvious. When temperature beyond 300°C , increasing trend of ethanol slow down. The content of ethanol and propanol is decreasing when temperature beyond 350°C . It is also verified that synthesis of alcohol is an exothermic reaction mentioned in above theoretical calculation. Over-high temperature is not appropriate for reaction. Yield of alcohols compounds increase rapidly with temperature increasing (below 350°C) and decrease when over 350°C . It is mainly because of ethanol decrease greatly. It is helpful for reaction to rise temperature on lower stage. On the contrary, too high temperature will reduce conversion and obstruct the reaction. Here we choose $T=350^{\circ}\text{C}$ as optimal reaction temperature.

C. Influence of Airspeed on Results

Pressure is 5.5MPa, temperature is 350°C , airspeed is $3000\text{h}^{-1}\sim 8000\text{h}^{-1}$, $\text{H}_2/\text{CO}=2$, reaction time is 16h, other parameters are the same. The results are as follows:

airspe ed h^{-1}	Space-ti me yield $\text{g}/(\text{ml}\cdot\text{h})$	selecti vity of C_2^+ alcohol %	Alcohol distribution wt%				
			carbi nol	etha nol	propa nol	buta nol	Total alcoh ol conte nt
3000	0.13	8.6	19.8	43.24	17.27	5.61	85.92
4000	0.51	35.73	14.83	43.40	19.72	6.93	84.88
6000	0.53	40.51	10.56	47.32	20.85	8.27	87
8000	0.46	30.25	6.53	39.58	18.96	7.19	72.76

According to above experimental results, we can obtain trend chart of parameters in the above-said conditions such as CO conversion, C_2^+ alcohol selectivity, proportion of all kinds C_2^+ alcohol in the products and so on.

Fig 8 influence of airspeed distribution on C_2^+ alcohols productFig 9 influence of airspeed distribution on C_2^+ alcohols yield

As shown in above figures, changing airspeed can influence the content of ethanol, propanol and butanol, but it is not obvious. Therefore, pressure and temperature plays more important role on the yield of C_2^+ alcohol. There is a lower yield of alcohol when airspeed is $3000h^{-1}$. This is because the gas through catalyst for a long time when airspeed is lower, result in the increasing of side effects and by-products. First, lead to further reaction of part alcohols substances for by-products. Secondly, too long reaction time will cause the increase of carbon deposition and lead to catalyst poisoning. This is also one of the important reasons for low yield. When airspeed exorbitant ($8000h^{-1}$), yield of alcohols reduce and the content of ethanol, propanol and butanol decrease. This is because time which gas through catalyst is too short and reaction is inadequate. Here we think airspeed should be controlled between $5000h^{-1}$ and $6000h^{-1}$, and take $6000h^{-1}$ as optimum reaction airspeed.

D. End Gas Detection

According to above experimental process, detect the end gas with repetitive conditions that pressure is 5.5MPa, temperature is $350^{\circ}C$, airspeed is $6000h^{-1}$, H_2/CO is 2 and reaction time is 16 hours. Collect gas respectively at 10h, 12h, 14h, 16h, and then analyze its components by gas chromatographic. The results are as follows:

Reaction time h	$H_2\%$	$CO\%$	$CO_2\%$	$CH_4\%$	$C_2H_4\%$	$C_2H_2\%$
10	26.88	30.41	18.06	12.65	0.39	0.37
12	26.54	27.12	19.46	14.9	0.15	0.36
14	26.22	25.26	21.01	16.98	0.14	0.37
16	24.97	25.05	22.22	17.48	0.14	0.36

Known as the experimental results, the content of CO_2 and CH_4 is increasing and H_2 and CO is decreasing in process of time. It means the reaction is more adequate. For 14h and 16h, although the content of each substance is still change, trend is gentle. It means the reaction is already close to equilibrium. Content of H_2 and CO in end gas is higher, although the conversion is relatively high, they still not react completely. This is because of higher airspeed. It can be improved by

reducing airspeed, but lower airspeed will lead to side reactions increasing. So we think relatively rational method is that make a second cycle for collecting end gas to improve the use ratio of H_2 and CO .

CONCLUSIONS

This paper firstly analyzes influence of parameters to synthesis theoretically from the synthetic mechanism of C_1-C_5 alcohols. Too low temperature will reduce reaction activity and too high will hinder synthesis. Alcohols selectivity and yield increase with pressure increasing. But excess pressure goes against equipment production and test devices processing and increase the cost. Increasing the content of H_2 in input gas can improve conversion of CO . But high content of H_2 will lead to CO too little, thus decrease alcohol content. Low inert gases may hinder synthesis, but the impact is not obvious.

Do the synthesis experiment in different process parameters. Validate correctness of academic trend and finally determine the optimum technological conditions: $P=5.5MPa$, $T=350^{\circ}C$, airspeed= $6000h^{-1}$. Provide technical guidance for future industrialization.

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